Chitosan-based delivery systems for plants: *A brief overview of recent advances and future directions*

Muhammad Mujtaba[1], Khalid Mahmood Khawar[2], Marcela Candido Camara[3], Lucas Bragança Carvalho[3], Leonardo Fernandes Fraceto[3], Rania E. Morsi[4,5], Maher Z. Elsaabe[7], Murat Kaya[6], Jalel Labidi[8], Hidayat Ullah[9], Depeng Wang[10*]

[1]Institute of Biotechnology, Ankara University, Ankara 06110, Turkey

[2]Ankara University, Faculty of Agriculture, Department of Field Crops, 06100 Ankara, Turkey

[3]São Paulo State University (UNESP), Institute of Science and Technology of Sorocaba, Department of Environmental Engineering, Sorocaba, Brazil

[4]Egyptian Petroleum Research Institute, Nasr City, 11727, Cairo, Egypt

[5]EPRI-Nanotechnology Center, Egyptian Petroleum Research Institute, 11727 Cairo, Egypt

[6]Department of Biotechnology and Molecular Biology, Faculty of Science and Letters, Aksaray University, 68100 Aksaray, Turkey

[7]Department of Chemistry, Faculty of Science, Cairo University, 12613 Cairo, Egypt

[8]Biorefinery Processes Research Group, Department of Chemical and Environmental Engineering, University of the Basque Country (UPV/EHU), Plaza Europa 1, 20018 Donostia-San Sebastian, Spain

[9]Department of Agriculture, The University of Swabi, Anbar 23561, Swabi, Khyber Pakhtunkhwa, Pakistan

[10]College of Life Science, Linyi University, Linyi, China

*Corresponding author

Depeng Wang

Address: College of Life Science, Linyi University, Linyi, China

E-mail: wyandywang@163.com
wangdepeng@lyu.edu.cn

Tel: +86-0539-7258717

Abstract

Chitosan has been termed as the most well-known of these biopolymers, receiving widespread attention from researchers in various fields mainly, food, health, and agriculture. It is a deacetylated derivative of chitin, mainly isolated from waste shells of the phylum Arthropoda after their consumption as food. Chitosan molecules can be easily modified for the adsorption and slow release of plant growth regulators, herbicides, pesticides, and fertilizers, etc. Chitosan as a carrier and control release matrix offers many benefits including; protection of biomolecules from harsh environmental conditions such as pH, light, and temperatures and slow, prolonged release of active ingredients from its matrix consequently protecting the plant's cells from the hazardous effects of burst release. In the current review, we will discuss the recent advances in the area of chitosan application as a control release system. In addition, future recommendations will be made in light of current advancements and major gaps.

Keywords: Chitosan nanoparticles; slow delivery; phytohormones; plants

1. Introduction

Advancements in the field of nanotechnology open up new doors in terms of applications for various nanomaterials in different fields including plant sciences. The application of different biomaterials as delivery systems showed many advantages like biocompatibility, nontoxicity, an affinity for biomolecules, efficient encapsulation, prolonged release, etc. [1, 2]. Agriculture science is confronted by a number of challenges such as nutrient losses, pathogens, and low crop yield due to water, fertilizer and pesticide mismanagement [3]. To manage such problems, farmers are using intensive amounts of pesticides and other agrochemicals (nitrogenous, phosphoric, potassic fertilizers and organometal) which are ultimately leading to environmental problems such as air pollution, soil toxicity, degradation of agro-ecosystems, residue accumulation and pesticide resistance in insects and pathogen as well as human health problems. In order to overcome the described problems due to the indiscriminate use of synthetic agrochemicals, it is important to develop new strategies for the safer and effective application of these chemicals.

It has been shown by many researchers that controlling the release of agrochemicals (fertilizers, pesticides, fungicides, and herbicides) can lead to higher activity and enrich the soil content of the natural biodegradable components [4]. That is how the new smart materials (the nanomaterials) can play a crucial role in enhancing the agricultural process [3, 5-9].

Considering the recent advancements in nanotechnology, encapsulation of ingredients such as pesticides, herbicides and nutrients can be termed as the most favorable solution to the current challenges [6, 10, 11]. Recently the utilization of nano-carriers and nanosensors has drawn the attention of researchers from divergent fields of plant sciences and extensive research efforts are underway to enhance the synthesis and efficiency of biopolymers based on nanocarriers [12, 13]. What characteristic of nanomaterials makes them so effective in improving crop production? Primarily their size. The small molecular size can easily penetrate the plant surface membrane through the cuticles, trichomes, stomata, stigma, hydathodes, wounds and root junctions [14, 15]. For example, controlled release of agro nutrients from nanocarriers enhances the efficacy of the active ingredients, reduces the loss by decreasing the volatilization and prevents contamination risks (environmental and health). The desirable properties of biomaterials based nanocarriers are the reason behind the growing interests in their applications for plants [16]. A wide range of biopolymers including cellulose, chitin, chitosan, collagen, alginate and starch have been actively applied as nanocarriers for the controlled delivery of agrochemicals [12, 17]. The use of cellulose was not as extensive as starch or lignin derivatives [18]. A set of criteria has been defined for a polymer matrix intended to be used as a microencapsulation agent [19].

i. The biopolymer must have a glass transition state, molecular weight and molecular structure suitable for the release (prolonged) of the load.
ii. The surface functional groups should not react with the loaded content (agrochemicals etc.)
iii. It should be biodegradable and non-toxic to the environment.
iv. The polymer should have enough stability during storage and application and should be economical.

A large number of studies have been conducted on the encapsulation of antimicrobial agents, pesticides, agrochemicals and agro-nutrients to define the required dosage for specific plants or crops to inhibit microbial growth, diseases or stresses. But, this does not solve the problem completely because the problem is linked to the application of synthetic agrochemicals [20]. Since the last decade, a hunt for an alternative, natural, economical, biodegradable and nontoxic carrier for agro nutrients and agrochemicals has been underway.

Chitosan has emerged as a potentially applicable polysaccharide in agriculture, medicine, cosmetic and biomedical industry for different applications [21, 22]. In plants, chitosan is gaining attention as one of the most suitable carrier matrices for agro-nutrients and agrochemicals, owing to its wide range of properties including biocompatibility, biodegradability, high permeability, cost-effectiveness, non-toxicity and excellent film-forming ability [23]. Chitosan and its derivatives, alone or in the composite form, are being used for the controlled release of pesticides, macro and micronutrients, herbicides and plant hormones [20]. An overview of current research shows that the number of articles in this area has been increasing which is a sign of growing interest of researchers in this field.

In this review, we will discuss the current status of chitosan application as a nano-carrier in agricultural science. In addition, we will provide a future perspective explaining the gaps in the research with possible solutions moving forward.

2. Overview of chitosan

Chitosan is a polycationic polymer isolated after the deacetylation of chitin. Chitin is a structural polymer of many organisms such as crustaceans, insects, mollusks, fungi, and shrimps, etc [24, 25]. The detailed compilation of chitosan sources has been given in Table 1. Chitin a very similar polymer to cellulose, as they function the same; structural integrity (Fig.1). Plants produce cellulose in their cells and chitin has been produced by crustaceans and arthropods in their shells. Up to now, three crystallographic forms of chitin have been reported as alpha (α), beta (β) and gamma (γ) [26]. The *α* and *β* are the most commonly existing forms of chitin and can be extracted from a variety of organisms. However, the sources of gamma chitin are scares and hard to find for mass production. For a long time all the literature was relying on a single article for the existence and knowledge of physicochemical properties of gamma chitin [27]. But a very recent report clarifies the big picture and answered a number of questions which were remained unanswered in the previous report [26]. Chemically it is a linear polymer consist of 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose monomers linked through 1–4 bonds. Structurally, *α* and *γ* are similar in terms of physicochemical properties compared to the β form of chitin. Compared to chitin chitosan is more functional, thanks to its amino based functional groups stretching along the chain [21]. The molecular weight, biological and physicochemical properties and purity of the isolated chitosan mainly depend upon the source and extraction method [28]. In addition, the protonation intensity of amino groups also plays a vital role in the functionality of chitosan. The major properties of chitosan include nontoxic for humans (LD50=16 g kg^{-1} in rat) mucoadhesive [29], hemostatic, film-forming [30], excellent adsorption matrix, antiviral, antibacterial and antifungal [31], antioxidative [32]anticholesterolaemic agent [33]. Literature lists multiple references dealing with the properties and wide range applications in the fields of biology, medicine, agriculture, and other vital areas [34]. All the above-mentioned properties of chitosan make it a suitable candidate for myriads of application in different fields including, medicine, cosmetics, and agricultural sciences.

Table 1. Aquatic, terrestrial and microorganisms sources of chitin and chitosan (Reprinted from [25]).

Aquatic	Terrestrial	Microorganisms
Crustaceans	Arthropods	Fungi (cell walls)
Crab	Spiders	Ascomydes
*Chionoecetes opilio***[35]**	*Geolycosa vultuosa* [39]	*Mycelium*[41]
*Podophthalmus vigil***[36]**	*Hogna radiate* [39]	
*Paralithodes amtschaticus***[37]**	*Nephila edulis* [40]	*Penicillium* [42]
Carcinus mediterraneus **[38]**		Yeast (b type)[43]
		Blastomycota
	Scorpions	Blastocladiaceae [44]
	Mesobuthus gibbosus [46]	
		Chytridiomycota
Water lobster		Chytridiaceae [24]
Crayfish **[47]**	Insects	
	Ants	
		Protista
Prawn	Beetles	Brown algae [45]
Aristens antennatus **[48]**	*Bombyx mori [49]*	Planta
Krill	*Holotrichia parallela*	
Daphnia longispina **[50]**	*Leptinotarsa decemlineata*	Green algae [45]
Anax imperator **[51]**		
Hydrophilus piceus **[51]**		
Notonecta glauca **[51]**	Cockroaches	
Agabus bipustulatus **[51]**		
Asellus aquaticus **[51]**		
Mollusca		
Squid pens		
Loligo **[52]**		
*Todarodes pacificus***[53]**		
Coelenterata		

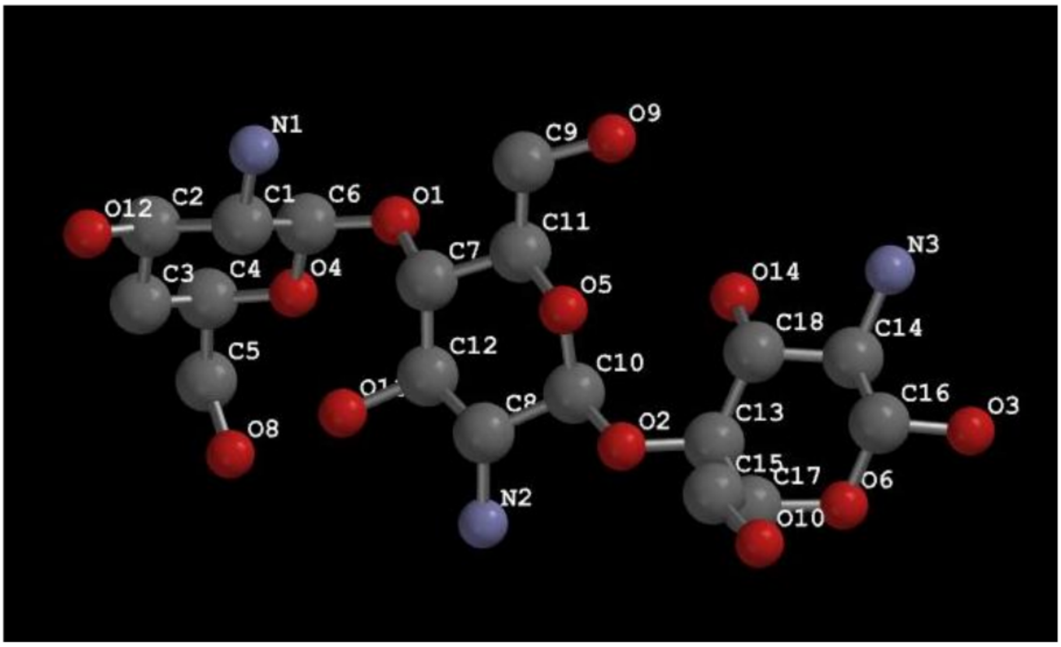

Figure 1. Chemical structure of chitosan; showing all amino groups in blue (Reprinted from with permission from MDPI from Sharif, Mujtaba, Ur Rahman, Shalmani, Ahmad, Anwar, Tianchan and Wang [25]).

3. Chitosan as a matrix for control release

After World War II, the agriculture sector had mainly started relying on synthetic pesticides. According to a report, only 0.1 % of the pesticides and other agrochemicals reach the target while the remaining have entered the environment through leaching or evaporation causing contamination for both humans and animals [54]. Control release can be defined as ''*the permeation-regulated transfer of an active ingredient from a reservoir to a targeted surface to maintain a predetermined concentration level for a specified period of time*''[55]. A control release matrix can maintain the release of active compounds, in this case, is synthetic pesticides, for a longer time. Additionally an effective release matrix can act as a reservoir for the load and protecting it from degradation mainly due to environmental factors such as UV radiations, water, evaporation, harsh pHs, etc [54]. The main objective of a nanocarrier for plants is the prolonged release of load, enhanced efficacy, and safety of the load and reduction of contamination. The concept of microencapsulation evolved in the late 1980s as an alternative to liposomes for solving the problem of stability as liposomes were unstable in biological solutions [56]. In the following years, researchers focused their attention on exploring and designing different matrices for control release through encapsulation. Chitosan became a dream polymer for encapsulation applications due to its surface amine-based functional groups stretching across the chain. Chitosan can form films, hydrogels, scaffolds, fibers and micro- and nanoparticles thanks to deacetylated surface making easier for myriads of modifications [57, 58]. With the increasing importance of control release in plants, chitosan has been emerged as an ideal polymer due to its desirable physicochemical and biological properties. Since chitosan-based NMs control the release of active ingredients such as pesticides, micronutrients, and plant hormones, they have become rather popular and are being produced in great amounts and marketed around the world. They are now an important part of the defense systems against plant diseases and crop growth promotors [59-65]. Several international organizations; the Codex Alimentarius, a joint body of the UN World Health Organization (WHO) and Food Agriculture Organization (FAO), the European Union (EU) and other organizations have introduced the concept of acceptable maximum residual levels of pesticides (MRLs) in order to confirm the acceptable levels of food quality [4]. Based on its biodegradability, chitosan-based nanomaterials are advantageous over the synthetic agrochemicals, since they are able to escape some stringent regulation of nanomaterials applications [66]. Considering the desired features of chitosan, it can be stated that chitosan-based nanocarriers have a bright future ahead in the field of control delivery in plant sciences.

4. Production of chitosan nanocarriers

Chitosan nanomaterials were prepared for the first time in 1994 by emulsification and cross-linking method as drug carriers [67]. Then after, other methods have been developed as ionic gelation [68], reverse micellar method [69], precipitation [70], sieving [71], emulsion droplet coalescence [72] and spray drying [73] most of them have been developed for pharmaceutical and medical fields [66] (Table 2). The production methods mainly depend upon the mode of action needed, for example, the release rate of the active ingredient will depend on the size and shape of the nanoparticles, the thermomechanical behavior and the level of toxicity of the degradable residues [23, 74, 75]. Ionotropic gelation is a simple and mild procedure that uses no chemical cross-linking reducing thus the possible toxic side effects of chemicals or reagents used in the procedure. The emulsion cross-linking method [20, 76] provides high loading capacity and better particle size and release control. Emulsion-droplet coalescence method [72] results in small particle size with high loading capacity. Precipitation method [77] does not involve toxic solvents and leads to better control of particle size and controlled release of the active materials. Reverse micellar method [74] is generally a tedious and laborious process but it has the advantage of producing suitable particle size with a small polydispersity index. The sieving process [71] uses a nano-scaled release device, however, it produces irregular particle sizes. Spray drying method gives a powder formulation with good entrapment efficiency, prolonged active ingredient release however, a lot of parameters can influence the final product particle size [70]. The ionic gelation method which is based on the ionic interactions between the positively charged chitosan and the polycationic negatively charged tripolyphosphate (TPP) is now among the most used method for the preparation of chitosan-based NMs and is recently has been adapted for agricultural applications. Several parameters control the size of the nanoparticles and consequently affects the plant responses towards the nano-chitosan, among these parameters are the degree of deacetylation (DD), molecular weight and concentration of chitosan, chitosan: TPP mass ratio, pH, temperature and rate of mixing of TPP and chitosan [78, 79] in addition to size distribution/polydispersity index (PDI), surface charge (zeta-potential) and functional/encapsulated component [78].

Table 2. Major advances in chitosan nanoparticles production protocols and applications.

Matrices	**Method**	**Encapsulated ingredient**	**Reference**
carboxymethyl chitosan modified carbon nanoparticles	Fast oxidation	Carbon nanoparticles	[80]
Tebuconazole metal-organic framework/chitosan	Coating	Tebuconazole metal-organic framework	[81]
Chitosan	Emulsion	Glyphosate	[82]
N-deoxycholic acid-O-glycol chitosan	Reverse micelles	Rotenone	[83]
N-hexanoyl-O-glycol chitosan	Reverse micelles	Atrazine	[84]
Chitosan nanocapsules	Ionotropic gelation	Achillea millefolium essential oil	[85]
Chitosan	Coating	Pesticide/diatomite/Fe3O4	[86]

N,N-dimethylhexadecyl carboxymethyl chitosan	Isopropanol agitation	Rotenone	[83]
chitosan	Emulsion	Imazamox	[87]
Pectin, chitosan, and sodium tripolyphosphate	Ionotropic gelation	Paraquat	[88]
Chitosan nanoparticles	Ionic gelation	S-nitrosoglutathione	[89]
Chitosan nanoparticles	Ionic gelation	Salicylic acid	[90]
Chitosan nanoparticles	Ionic gelation	Hexaconazole	[91]
Chitosan nanoparticles	Emulsion crosslinking	Cymbopogon martinii Essential Oil	[92]
chitosan (CS) nanoparticles		Nitrogen, phosphorous and potassium	[93]
chitosan (CS) nanoparticles	Spray drying	Cu	[64]

5. Chitosan as a controlled delivery system

5.1 Delivery of plant growth promoters

Phytohormones are molecules responsible for promoting plant growth and development. They are applied to crops to improve production, visual and nutritional aspects, alleviate biotic and abiotic stresses, and increase product shelf life. Although these molecules show the potential to be applied in many crops, few carriers have been explored as a matrix for plant growth promoters. Some examples of plant growth promoters coated in the chitosan matrix are described in Table 3. A carrier system composed of chitosan (CS) and γ-polyglutamic acid (CS/PGA) was developed for gibberellic acid (GA_3) delivery [94]. This system presented homogeneous particle size distribution (134 nm) and the GA_3 encapsulation efficiency was 61%. In other work [95], the same author's proposed chitosan/alginate (CS/ALG) and chitosan/tripolyphosphate (CS/TPP) nanocarriers for GA_3 encapsulation. The GA_3 encapsulation efficiency was higher than CS/PGA, reaching 100% CS/ALG and 90% CS/TPP. For the three carriers tested it was possible to observe that the encapsulation of GA_3 prevented its degradation and allowed the controlled release of the active materials when compared with the free hormone. Maximum GA_3 release was reached after 48h, 17h, and 10h, for CS/PGA, CS/ALG, and CS/TPP, respectively (Figure 2). These authors also performed biological activity assays on beans to evaluate the effects of free and encapsulated GA_3 on plant growth. The CS/PGA was more efficient than free GA_3 in stimulating seed germination, root and shoot growth, promoting an increase of 15-45% in the shoot length of beans plants. The CS/ALG showed significant effects on beans leaf development and in carotenoids levels compared to free GA_3 and CS/TPP nanoparticles. However, no differences were observed in relation to shoot growth between them

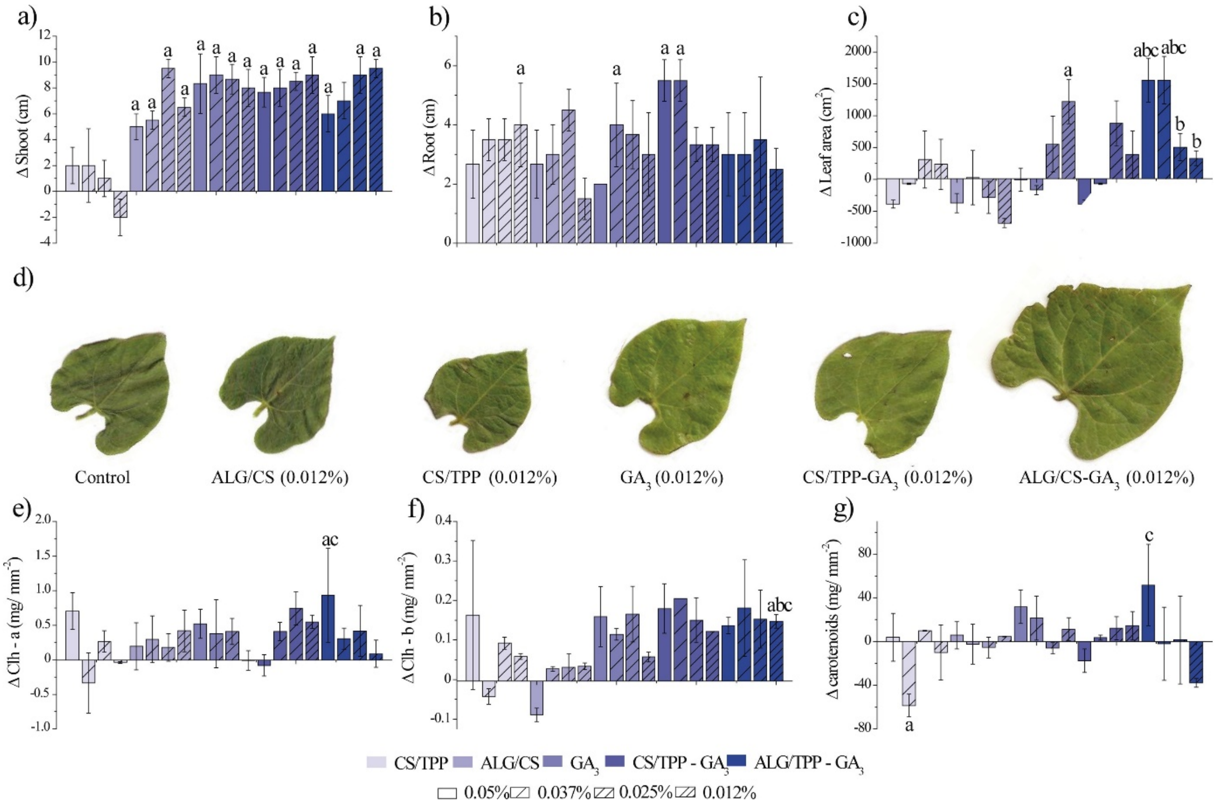

Figure 2: Biological activities of the alginate (AL)/chitosan (CS)-GA_3 and CS/TPP-GA_3 nanoparticles towards *Phaseolus vulgaris*: a) shoot development (cm); b) root development (cm); c) leaf area development (cm^2); d) images of the leaves for the treatment at a concentration of 0.012%; e) chlorophyll 'a' content ($mg\ mm^{-2}$); f) chlorophyll 'b' content ($mg\ mm^{-2}$); g) total content of carotenoids ($mg\ mm^{-2}$). Statistical analysis using one-way ANOVA (Reprinted with permission of Elsevier from Santo Pereira, Silva, Oliveira, Oliveira and Fraceto [95].

Salicylic acid (SA) is another important phytohormone responsible for plant defense response. Chitosan has been used as a matrix for the synthesis of SA nanoparticles to alleviate abiotic stress caused by heavy metals in *Isatis cappadocia* [96]. The CS/SA nanoparticles application could improve plant growth and phytoremediation efficiency under metal stress by helping plant roots build efficient barriers restricting the entrance of toxic compounds into the xylem, and thus reducing its translocation into shoots [96]. SA microencapsulation using chitosan from crustaceans' residues was developed by Martin-Saldaña, Chevalier, Iglesias, Colman, Casalongué, Álvarez and Chevalier [97]. The microparticles (1.57 µm to 2.45 µm) were obtained through the gelation method and showed encapsulation efficiency ranging from 59-99%. The lowest efficiency was obtained using the highest concentration of SA, which according to the authors, can be explained by the competitive interaction between TPP and SA to bond with CS. The bioassay on lettuce seedlings showed that low doses of chitosan-SA microparticles can favor the growth of lettuce root and induce defense proteins, and therefore are a promising formulation for activating the defense response of horticultural plants.

Nanoparticles with micronutrients like manganese, boron, copper, iron, zinc can be used as plant growth promoters and for soil nutrition [23]. As described by Choudhary and co-workers [98], CS nanoparticles coupled with copper show the ability to improve plant growth even under disease conditions. This is mainly correlated to the strong fungicidal activity of copper and its important role in electron transfer and redox reactions, boosting plant growth. In addition, chitosan is also an inducer of defense response in plants, helping in plant protection. The CS as micro- or nano-carrier for plant growth promoter delivery presents great potential to be used in agriculture, and thus, could be further explored.

5.2 Delivery of fertilizers

Soil fertilization is a common practice in agriculture to supply macro and micronutrients to crops, improving their quality. However, when in excess, they result in environmental contamination, increasing the salinity and unbalancing the pH of the soil [99]. Moreover, large amounts of nutrients may be lost prior to absorption by plants. To avoid these problems, chitosan micro- or nanoparticles and hydrogels have been studied as a strategy to enhance the efficiency of fertilizers, reduce soil contamination and promote a sustainable release of these molecules on the soil. Nitrogen, potassium, phosphate, copper, zinc, and vitamins were the focus of many pieces of researches in the last five years (Table 3). Chitosan-urea nanoparticles were successfully synthesized and characterized by Araújo and co-workers [99]. Their work describes a controlled release system for urea delivery using an interaction between humic substances and urea, loaded into chitosan nanoparticles. NPK nano fertilizers were prepared by ionic gelation method using chitosan [100]. The biological activity on coffee seedlings showed a significantly increased in nitrogen and potassium content in the leaves, which the suitable doses of NPK nano fertilizer for improvement of nutrients uptake were of 30 to 40 ppm. The nano fertilizer also enhanced the contents of chlorophyll and carotenoids, and using doses of 30 ppm, the NPK-nanoparticles stimulated the growth of coffee seedlings[8]. In 2016, Abdel-Aziz and co-workers [101] studied the uptake and translocation of chitosan/NPK nanoparticles in wheat seedlings. They discuss that the nanoparticles entered in the stomata of the leaves and were translocated by the phloem system, which is the main and unique pathway for translocation of nanoparticles and in consequence, are carried out to shoots and roots, improving plant development.

Hydrogels films were another strategy adopted for fertilizer delivery. Hydrogel shows the ability to gradually release their load material in the environment through water absorption [102]. Iftime, Ailiesei, Ungureanu and Marin [103] designed a controlled release system for urea by hydrogelation of chitosan with salicylaldehyde. The aim of the authors was to promote soil fertilization and water retention. The water absorbency capacity of the formulation was 68 g/g and water holding capacity in the soil about 154%. The release of urea was carried out in three stages, firstly, releasing 46% in 5h, then a slowed release reaching 75% after 11 days, and lastly, slower continuous release in the next 23 days when almost all the urea was released. In addition, due to the increment of nitrogen in the soil, a growth of over 70% in tomato plants was observed in treated soils, when compared to untreated ones Figure 3.

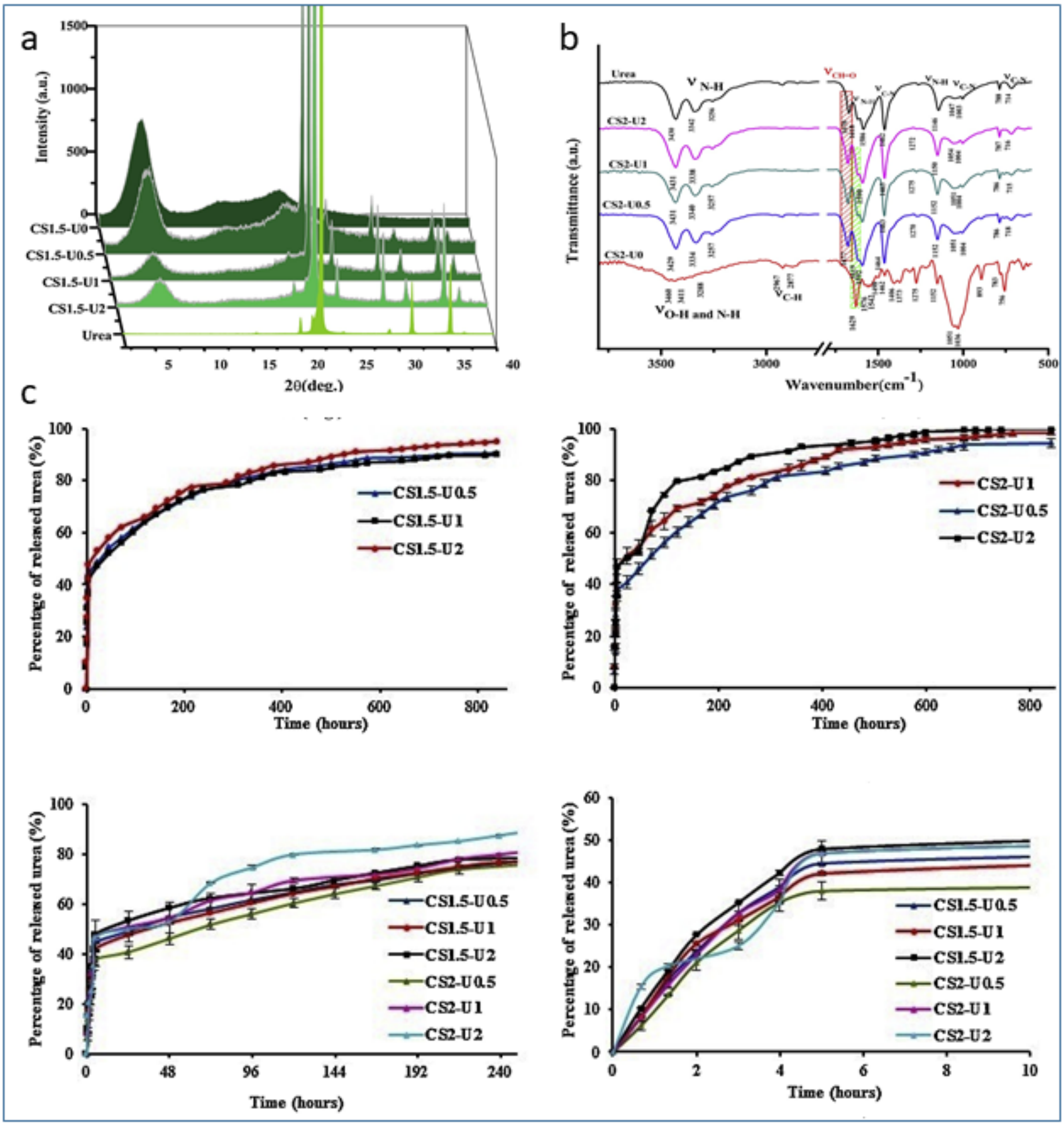

Figure 3: a) X-ray diffractograms of the formulations, b) FTIR spectra of a series of formulations and c) Percentages of urea released during 35 days from the formulations detailed for the first 10 days and first 10 h (Reprinted with permission of Elsevier from Iftime, Ailiesei, Ungureanu and Marin [103]).

Biofertilizers based on living microorganisms can be applied to seeds or soil, where bacteria or rhizobacteria colonize the plant rhizosphere and improve its growth. In this context, Perez, Francois, Maroniche, Borrajo, Pereyra and Creus [104] proposed ionically crosslinked beads composed of chitosan and starch to coat *Azospirillum brasilense* and *Pseudomonas fluorescens*. The authors produced microbeads around 1.82 mm, which remained relatively stable for the period of one year. This polymeric matrix loaded with plant growth-promoting bacteria was capable to release viable cells in a fast and prolonged manner on the non-sterile soil. Therefore, biofertilization is also a promising alternative practice to contribute with sustainable agriculture and to the recovery of poor-quality soils.

5.3 Delivery of genetic materials

The development of nanocarriers to deliver genetic materials, such as plasmid DNA, siRNA, proteins and double-stranded RNA or DNA, into protoplasts or plant cells, opens new opportunities in plant genetic engineering. This pioneer area still must face important challenges, including genetic insertion safety and nano-plant-gene interaction to ensure popular acceptance [105]. Chitosan is a potential carrier to gene delivery and plant transformation due to its capability to complex with negatively charged genetic material via electrostatic interactions, protecting against enzymatic degradation [106, 107]. Kwak, Lew, Sweeney, Koman, Wong, Bohmert-Tatarev, Snell, Seo, Chua and Strano [106] developed a chloroplast-target transgene delivery by the complexation between plasmid-DNA with chitosan-complexed single-walled carbon nanotubes. The system was able to penetrate through the protoplast and chloroplast membranes of the arugula plants showing an estimated efficiency of pDNA delivery of 47%. The complexation with chitosan also protected pDNA from cellular degradation, and it was demonstrated that the nanoparticle-mediated delivery approach could also be applied to other plant species such as watercress, spinach, and tobacco plants.

5.4 Delivery of pesticides

The excessive use of pesticides was a traditional way of fighting pests and microbes in a trail to increase crop yields, however, the excess pesticides were a major threat to the humans and animals who consume the agricultural products, in addition to a contamination of the underground water, This was a challenging problem which was a concern of a great number of researchers. How to control and optimize the amount and rate of release of the pesticides in the agricultural industry? Chitosan is a versatile polysaccharide that has enabled the development of intelligent systems for pesticide release in agriculture, favoring the reduction of the consumption of hazardous compounds and reducing environmental and human health impacts. The new work has produced asset release systems responsive to the environmental or intrinsic conditions of its target. Efforts are also made to increase formulation loading and the production of controlled release carriers that promote protection against photosensitive and highly volatile compounds. Relevant work in recent years is shown in Table 3 and some of them are reported in more detail below.

Chitosan-Isoleucine-based nanomicellar systems and copolymers were developed to encapsulate the spinosad fungicide, whose results indicated effective protection against photodegradation [108]. The association with nanomicella promoted an active release was faster at pH 6.4 than at pH7, indicating the formulation is pH-responsive, and the activity showed higher activity against fungi treated with the encapsulated formulation compared to unencapsulated spinosad. He and coworkers coated crystals of *Bacillus thuringienses* with chitosan and observed that chitosan improves the stability and resistance of these crystals to environmental stress and is responsive to alkaline pH, indicating its potential to fight specific insects in their larval stage as it may release the active in the environment. midgut of these pests [109]. Paula, Sombra, de Freitas Cavalcante, Abreu and de Paula [110] synthesized chitosan/cashew tree gum microspheres loaded with *Lippia sidoides* (LS) essential oil, as a natural insecticide. A slow release of the LS was achieved only after the microspheres have been crosslinked. In this way, the loaded spheres are efficient pest control. Guan, Chi, Yu and Li [111] prepared chitosan/alginate beads loaded with imidacloprid a photodegradable insecticide. The rate of the insecticide release from the beads was much slower than that of the free insecticide (Figure 4). The rate of release was a function of alginate: chitosan ratio. Chitosan derivative containing hydrophilic and hydrophobic groups was prepared and it forms spherical micelles with a size of 167.7–214.0 nm by self-assembly in aqueous solution [112]. Rotenone, a water-insoluble botanical insecticide, was loaded into the micelles solution by reverse micelle method in much higher concentration than in aqueous solution. This assembly provided a successful vehicle for the controlled release of pesticides into the soil.

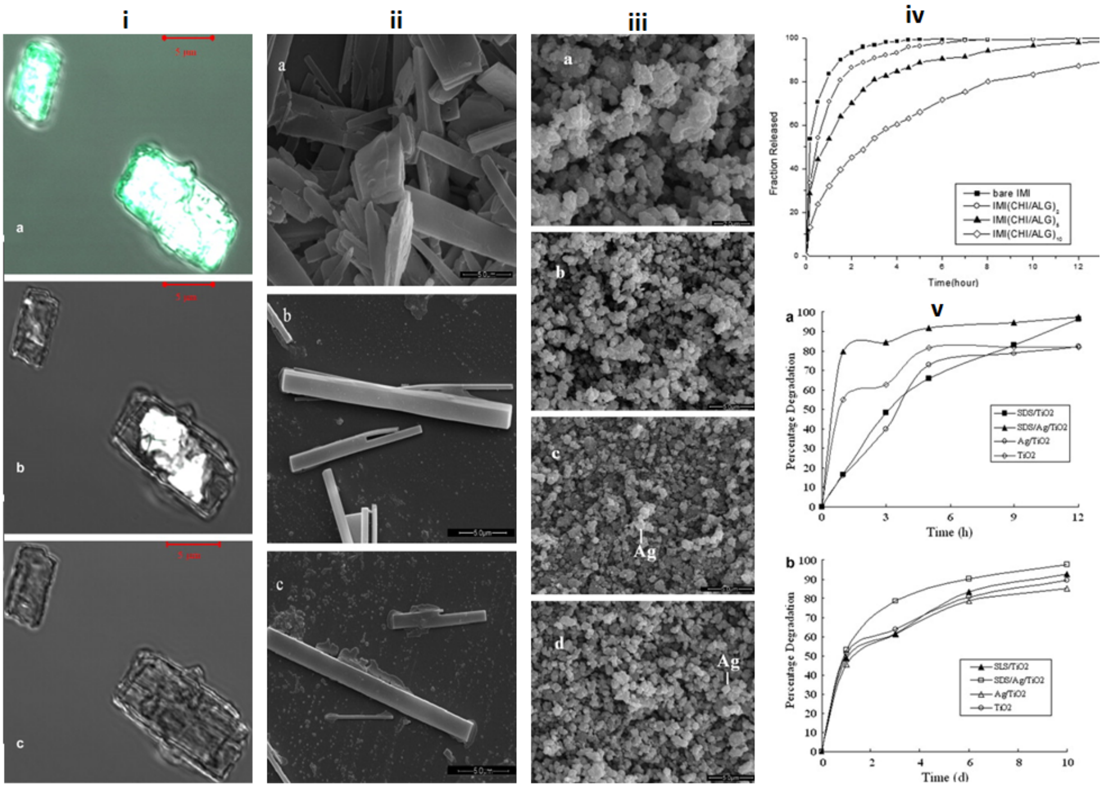

Figure 4: i) Transmission CLSM images of the imidacloprid release process from the Chitosan/Alginate (CHI-ALG)$_{10}$ microcapsules. (a) Morphologies of imidacloprid microcrystal before dissolution. (b) Images of imidacloprid microcrystal in dissolution. (c) Images of polysaccharide capsules after removal of the crystal cores; ii) SEM images of IMI microcrystals (a) uncoated, (b) coated with 5 layers of CHI/ALG, (c) coated with 10 layers of CHI-ALG; iii) SEM micrographs of photocatalysts: (a): TiO_2; (b) SDS/TiO_2; (c) Ag/TiO_2; (d) SDS/Ag/TiO_2; iv) *In vitro* dissolution profile of coated and uncoated imidacloprid microcrystals; v) The degradation of nano- imidacloprid on photocatalysts (a): catalyst powders under UV light; (b): catalyst powders under natural light (Reprinted with permission of Elsevier from Guan, Chi, Yu and Li [111]).

Chitosan coating on mesoporous silica nanoparticles may increase loading in pesticide formulations [113, 114]. A study by Liang and co-authors reached a loading value for prochloraz fungicide molecules of 25.4%. In addition to improving light stability, the study reported that acid and enzymes from infected fruits favor the release of the active ingredient present in the nanoparticles, characterizing them with this double responsiveness character [113]. The effectiveness of this system has been proven by improving antifungal activity against citrus diseases and reducing toxicity, in zebrafish assays, of six times the toxicity about the application of the isolated active. In the case of a synchronous system for encapsulating the emulsion-based azoxystrobin fungicide and modifying the surface of mesoporous silica nanoparticles, loading may be increased from 3.6% to 21% while maintaining pH-responsive release, which is controlled by the carboximethychitosan gatekeeper. The reported system showed a positive effect on late tomato pest, *Phytophthora infestans*, when compared to the active applied alone in the same dosages [114]. Metal-organic systems can be combined with chitosan to produce fungicidal nanocapsules, such as adsorbed charged tebuconazole and assembled by electrostatic interactions with chitosan and pectin. The study demonstrated that the release is responsive to the action of pectinase in slightly acidic medium, and the fungicide nanocapsules showed microbicidal efficacy and did not affect the growth of Chinese cabbage, providing evidence that they may be safe for application [115].

The association between chitosan and botanical compounds have also been reported in studies [116]. Plants produce compounds as defence mechanisms with the proven activity of these compounds, such as Carvacrol and Linalool which have insecticidal activity and repellents. The problem encountered with the use of botanicals in agricultural formulations is related to photosensitivity and high volatility. A study by Campos and co-workers reports the production of beta-cyclodextrin and chitosan nanoparticles for inclusion compound formation with linalool and carvacrol and suggests an improvement in the life of the compounds. The results indicate that the formulation enables a more sustained release in these actives, which were significantly more effective in terms of acaricidal activities and oviposition against *Tetranychus urticae* and enabling applications in an environmentally friendly manner by the use of natural compounds.

5.5 Delivery of herbicides

Herbicides are compounds traditionally used by agriculture to combat unwanted plants, classified as weeds, which cause yield losses. These compounds have their importance due to the growing demand for food, however, they pose risks to several organisms [117]. Technologies to improve the effectiveness of these molecules and reduce potential risks have been developed, such as the association of these compounds with chitosan. Important studies published in recent years (Table 3) demonstrate the potential of chitosan to be used in herbicide formulations.

Table 3. Examples of chitosan application as a polymeric matrix for agricultural compounds delivery.

Matrix	**Active ingredient**	**Properties**	**Benefits**	**References**
Cu-chitosan	Copper	MD: 361.3 nm ZP: +22.1 mV PDI: 0.20	Antifungal activity, induction of antioxidant and defense enzymes, and significant increasing in plant development	[64]
Chitosan/TPP (Sodium tripolyphosphate)	Salicylic acid	MD: 1.57-2.45 um PDI: 0.08-0.22 EE: 59-99%	Induction of lettuce plant defense response and growth	[97]
Chitosan/TPP	Salicylic acid	-	Improve plant defense to overcome metalloid stress caused by arsenic	[96]
Chitosan/Alginate	Gibberellic acid	MS: 450 nm ZP: -29 PDI: 0.3 EE: 100%	Improve the growth of bean plants and fruit growth of tomato	[94, 118]

Chitosan/TPP (Sodium tripolyphosphate)		MS: 195 nm ZP: +27 mV PDI: 0.3 EE:90%		
Chitosan/y-polyglutamic acid	Gibberellic acid	MS: 134 nm ZP -27.9 mV PDI 0.35 EE: 61%	Enhanced seed germination, root growth and leaf area, and avoid GA_3 degradation	[94]
Chitosan	Nitric oxide	MD: 38.81 nm ZP: +17.7 mV PDI: 0.30 EE: 91.07%	Alleviate salt stress in maize plants preventing negative effects on plant growth	[119]
Chitosan/TPP	Zinc	MD: 250-300 nm ZP: +42.34 mV PDI: 0.28 EE: 10-40%	Overcome zinc deficiency in poor soils, prevent nutrient loss and environmental pollution	[120]
Chitosan/sodium montmorillonite clay	KNO_3	EE: 40 - 65%	Continuous release of potassium for 60 days	[102]
Chitosan/TPP	Urea mixture with peat, humic acid or humin	-	Controlled release of urea by humic acid substances and by pH	[99]
Chitosan/ poly-methacrylic acid	NPK	-	Nanoformulation with the lowest concentration of NPK promoted greater wheat development	[101]
Chitosan/starch	Plant growth-promoting bacteria	MD: 2.97 nm	The hydrogel structure allowed a fast and prolonged release of bacteria in soil, which has strong biotechnological potential as biofertilizer	[104]
Chitosan/TPP	Thiamine	MD: 596 nm ZP: +37.7mV PDI <1	Thiamine nanoparticles improved chickpea seed germination and seedling vigor, as well as the content of IAA and defense enzymes	[121]

		EE: 90%		
Chitosan/TPP	KNO$_3$	EE: 92 - 136%	The systems showed a swelling-controlled mechanism to release the fertilizer on soil	[122]
Chitosan/ sodium montmorillonite clay				
Chitosan/starch/TPP	KNO$_3$	MD: 3.0 - 3.7 mm EE: 36-40%	The cumulative release of KNO$_3$ achieved 70-80% after 14 days, which was influenced by the presence of water	[123]
Chitosan/hydroxypropyl methylcellulose	KNO$_3$	-	The blend increased about 50 days the residence time of the fertilizer on soil	[124]
Chitosan/salicylaldehyde	Urea	-	The hydrogel promoted a sustained delivery of urea on soil, reaching maximum release after 35 days. Moreover, the formulation improves the water-holding capacity of the soil and stimulated tomato growth	[103]
Chitosan/TPP	-	MD: 259 nm ZP: 40.9 mV PDI: 0.281	Chitosan nanoparticles showed growth effects in wheat seeds and seedlings in low concentrations (5ug/mL) due to better absorption by seed surface and regulation of IAA synthesis	[125]
Chitosan/TPP	NPK	MD: 500 nm ZP: 50 mV	The nanoparticles showed a sustainable release of NPK during 240h. The application of nano fertilizer in coffee seedlings enhanced NPK levels in the leaves, which improved plant development	[100]
Chitosan/Polymethacrylic acid	NPK	MD: 24 - 87 nm ZP: 10 - 85 mV	The system was toxic when applied on *Pisum sativum* in highest doses, inhibiting root growth, lateral root formation and causing cell abnormalities	[93]

Chitosan/ Polydopamine	ZnPN	Film thickness: 50-70 nm ZP: -42.7 mV	The nanoparticles showed pH-responsive release profile, increased the nutrient utilization efficiency and improved corn seedlings growth	[126]
Chitosan/Polymethacrylic acid	Potassium	MD: 368 nm EE: 34.98%	The system showed a slow release profile fitting in the criteria for slow-release fertilizer	[127]
Chitosan/polyacrylic acid	Copper	MD: 4.8 - 10.7 nm ZP: -22.9 - +26.8 mV	The nanoparticles present antifungal and antibacterial activity and improved onion plants growth when treated with a concentration of 75 ppm	[128]
Chitosan	Urea	EE: 60 - 96%	The hydrogel was prepared using oxidized and grafted chitosan showing a swelling degree of 1500 to 2300%, being pH-dependent. The urea release is favored in alkaline soils	[129]
Chitosan-complexed single-walled carbon nanotubes	Plasmid DNA	MD: 104 – 190 nm ZP: 28.1 – 32.3 mV	Chloroplast transformation in *Eruca sativa, Nasturtium officinale*, *Nicotiana tabacum,* and *Spinacia oleracea* plants	[106]
Chitosan	Harpin$_{pss}$ protein	MD: 133.7 nm ZP: +48.6 mV EE: 89.7 %	Tomato plants treated with Harpin nanoparticles showed resistance against fungi disease caused by *Rhizoctonia solani*	[130]
Pectin/Chitosan/TTP	Paraquat	MD: 520 nm ZP: -16 mV PDI: 0.4 EE: 89%	Trial with corn and mustard plants demonstrated improved herbicidal activity. The herbicide nanoparticles showed reduced toxicity and mutagenicity to human cells, lower absorption, and deep soil penetration.	[88]
N-octyl derivates/chitosan	Atrazine	MD: 41-177 nm EE: > 90%	37.5% reduction in the use of organic solvents in herbicide formulations and promotes the slower release of the active.	[131]

Smectite/Chitosan/Fe(III)	Imazamox	-	Assays with *Brassica oleracea botrytis* have shown herbicidal activity similar to the commercial formulation, although the release is slower. However, there was a 15% reduction in total soil leaching losses and a 40% reduction in the maximum concentration in soil leachate.	[87]
Alginate/Chitosan	Imazapic and imazapyr	MD: 377 nm ZP: -30 mV EE: 62-71% 1.8×10^9 particles/mL	Increased herbicidal activity tested on *Bidens pilosa*. Slower release compared to isolated assets and reduced toxicity and genotoxicity.	[132]
Chitosan/TPP	Imazapic and imazapyr	MD: 478 nm ZP: +15mV EE: 58-70% 1.2×10^9 particles/mL	Increased herbicidal activity tested on *Bidens pilosa*. Slower release compared to isolated assets and reduced toxicity and genotoxicity.	[132]
Chitosan/TPP	Paraquat	MD: 282 nm ZP: +5 mV EE: 63%	The influence of humic substances promoted a reduction in the toxicity of encapsulated Paraquat compared to commercial.	[133]
Carboxymethyl/chitosan	Diuron	MD: 250 nm ZP: -30 mV PDI: 0.16 EE: 78%	Controlled release and Glutathione-responsive for herbicide release. Efficacy in pre-emergent target species (*Echinochloa crusgalli*) trials and preservation of non-target species.	[134]
Carboxymethyl chitosan/2-nitrobenzyl	Diuron	MD: 140nm ZP:-30mV EE: 91%	The micellar system was photoresponsive to herbicide release and kept it encapsulated in the absence of light.	[135]
Chitosan-Isoleucine/ copolymers	Spinosad	MD: 454 nm PDI: 0.2 ZP: +16 mV	Photodegradation rate reduction, pH-responsive, antifungal activity against pathogenic bacteria found in bananas.	[108]

Porphyrinic metal-organic/pectin/chitosan	Tebuconazole	MD: 158 nm ZP: +26 mV EE: 30%	The tebuconazole nanocapsules did not affect the growth of Chinese cabbage and had a dual microbicidal effect on plant pathogens, responsive to pH and pectinase action.	[115]
Mesoporous silica/carboxymethyl chitosan	Azoxystrobin	MD: 152 nm EE: 71% Loading: 21%	It presents pH-responsive release and improved fungicidal activity against late tomato pest, *Phytophthora infestans*.	[136]
Mesoporous silica/chitosan	Prochloraz	MD: 340 nm ZP: +35 mV Loading: 25%	Nanoparticles showed good properties responsive to esterase and pH, sustained antifungal efficacy against citrus pathogens and reduction of potential environmental damage.	[113]
Mesoporous silica/chitosan derivative	Pyraclostrobin	MD: 299 nm Loading: 40% ZP: 30mV	The coating of mesoporous silica nanoparticles increased loading from 26 to 40% and demonstrated the same half-dose fungicidal activity against *Phomopsis asparagi.*	[137]
Carboxymethyl chitosan/deoxycholic acid	Rotenone	spherical micelles MD: 91-140 nm EE: 60-98% Loading: 1-6%	Increase in the amount of water-soluble fungicide in the order of 50 times that of the isolated active, resulting in a reduction in the use of organic solvents.	[114]
Poly(2-dimethylamino-ethyl methacrylate)/chitosan	Pyraclostrobin	EE: 64% Loading: 19%	The microcapsules presented pH release and responsive term. Toxicity reduction in zebrafish assays.	[138]
Beta-cyclodextrin/chitosan	Carvacrol and linalool	MD: 175 and 245 nm ZP: +23 and +43 mV PDI: 0.1 and 0.3	Inclusion compounds between beta-cyclodextrin / chitosan essential oils and nanoparticles showed higher acaricidal activity and reduced oviposition against *Tetranychus urticae.*	[116]

		EE >90%		
Chitosan/alginate or carboxymethyl cellulose	*Bacillus thuringiensis*	Bipyramidal shape MD: 0,6x1,2 µm ~2x10^7 spore/mL	Protection of parasporal crystals from environmental stresses prolonging their activity. Toxins released at pH above 9.0 and larvicidal toxicity equivalent to unencapsulated crystal toxins.	[109]
Modified clay/chitosan/alginate	Acetamiprid	D: 1.2-1.7 mm Loading: 4-6% EE: 43-90%	Coating the chitosan clay increases loading and encapsulation efficiency for the slower released pesticide.	[139]
Alginate/chitosan	Acetamiprid	D: 201 nm PDI: 0.39 ZP: -32 mV EE: 62%	The formulation acts by releasing the pesticide in a controlled manner over a wide pH range.	[140]
Chitosan/TTP	hexaconazole	D: 100 nm ZP: +35mV EE: 73%	Effective in fungal control in alkaline soils, superior to the commercial formulation and less toxic in non-target cell lines.	[141]

MD: mean diameter; ZP: zeta potential; PDI: polydisperse index; EE: encapsulation efficiency; CE: crosslinking efficiency

Paraquat is a potent herbicide but has considerable toxicity and potential for environmental contamination in soils and water. The encapsulation of this compound in pectin/chitosan/TTP nanoparticles demonstrated that herbicidal activity could be improved concomitantly with the reduction of its toxic and mutagenic effects in human cells. Also in this study, it is shown that Pectin/Chitosan/TTP reduces the absorption and deep penetration of the herbicide in the soil, thus reducing the risks of contamination [88]. Grillo, Clemente, de Oliveira, Campos, Chalupe, Jonsson, de Lima, Sanches, Nishisaka and Rosa [133] and co-authors compared paraquat formulations under the influence of humic substances, the results showed that humic substances promoted a reduction in the toxicity of chitosan/TTP-encapsulated paraquat about the commercial formulation, due to changes in the dynamic equilibrium in the medium. Even in formulations where the association with chitosan-containing systems does not promote any increase in herbicidal activity, it can be maintained, and it is worth highlighting features that can be improved in these formulations. The smectite/chitosan/ Fe(III) combination, for example, promoted a slower release for the imazamox compound and maintained the herbicidal activity at commercial formulation levels, but reduced total soil leaching losses by 15% and by 40%. % concentration of leached herbicide, thus contributing to less soil contamination [87].

Studies involving chitosan and herbicidal molecules have also made efforts to demonstrate the advantages of this association for reducing toxicity and genotoxic effects. Alginate/chitosan and chitosan/TPP nanoparticles were employed for the formulation of slow-release nanoherbicides containing imazapic and imazapyr by Maruyama, Guilger, Pascoli, Bileshy-José, Abhilash, Fraceto and De Lima [132]. Herbicidal efficacy trials were tested against the target species *Bidens pilosa*, presenting higher efficacy than the isolated actives. For nano encapsulated herbicidal actives, cytotoxicity was reduced, less cell damage was identified in genotoxicity assays, and there was less interference in the amount and types of bacteria associated with the nitrogen cycle in the soil compared to the isolated actives [132]. Also, chitosan may be employed for the formulation of nanoherbicides responsive to a given stimulus [134]. Carboxymethyl/chitosan nanoparticles were glutathione-responsive for the controlled release of the diuron herbicide. The study showed that diuron release in vitro was dependent on glutathione concentration. Nanoformulation was effective in the preemergence treatment of target species and did not affect the development of non-target species. The use of carboxymethyl/chitosan micelles was combined with photolabile side groups of 2-nitrobenzyl and showed light irradiation sensitive herbicide release, indicating that reticulated micelles can be used as photo-controlled carrier system [140]. The use of chitosan, therefore, configures a promising alternative to produce intelligent and more efficient herbicidal formulations for use in agriculture.

6. Conclusion and Future prospects

Considering all the recent advancements made in the last five years in the application and production of chitosan-based nanocarriers, it can be stated that a major improvement has been made in this area. Yet, there is a lot still to achieve by advancing the production and application techniques of chitosan-based carrier matrices. The application of chitosan-based nanoparticles for control delivery purposes is still under research. Major constraints in transferring the chitosan-based delivery matrices for the control controlled release of pesticides, herbicides and other genetic materials to agriculture include;

1) Economical production techniques of nanocarriers (as the current synthesis procedures require time, money and labor),

2) Application of these nanocarriers for the dose reduction of already applied synthetic agrochemicals,

3) Guided delivery of agrochemicals through modified chitosan nanocarriers (ability to sense the target tissues of cells and release the load at the specific target),

4) An Intensive investigation of chitosan interaction with the plant's vascular system is required. It can help design the plant-specific or species-specific chitosan-based nanocarriers for the control release application.

5) Delivery of genetic materials through chitosan-based nanocarriers is still an expanding research area. A few number of articles have demonstrated the potential of chitosan nanocarriers for genetic materials. More research is required to fully explore the hidden potential of chitosan for carrying genetic materials in plants.

6) Lack of chitosan based nanocarriers available on the market for use in agriculture. For this reason, more detailed studies of chitosan-based carriers are needed.

7) The use of chitosan as nanocarriers in herbicide formulations has shown through studies that this technology improves the effectiveness of molecules and reduces potential environmental and human health risks. Existing studies with herbicides and chitosan are still considered

excipients, however, they direct to the potential application as controlled release systems and responsive to specific stimuli.

7) Advances in technology transfer to large producers and standardization of technology validation protocols are required to encourage the large production of these chitosan-based nano-formulations. It is also important to disclose this emergent technology with farmers, who will be the main buyers of the product.

In conclusion, new products based on chitosan nanoparticles should be further investigated and will corroborate with a sustainable development associated with possible economic and environmental gains.

Acknowledgments

The authors thank São Paulo Research Foundation (FAPESP, Grant Number #2017/21004-5 and #2018/23608-8) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Grant Number 301466/2018-1, 405623/2018-6 and 155959/2018-2) for financial support.

Reference

[1] P. Wang, E. Lombi, F.-J. Zhao, P.M. Kopittke, Nanotechnology: a new opportunity in plant sciences, Trends in plant science 21(8) (2016) 699-712.
[2] R. Raliya, J. Tarafdar, K. Gulecha, K. Choudhary, R. Rameshwar, M. Prakash, R. Saran, Scope of nanoscience and nanotechnology in agriculture, Journal of Applied Biology and Biotechnology 1(3) (2013) 041-044.
[3] L.R. Khot, S. Sankaran, J.M. Maja, R. Ehsani, E.W. Schuster, Applications of nanomaterials in agricultural production and crop protection: a review, Crop protection 35 (2012) 64-70.
[4] S. Kumar, M. Nehra, N. Dilbaghi, G. Marrazza, A.A. Hassan, K.-H. Kim, Nano-based smart pesticide formulations: Emerging opportunities for agriculture, Journal of controlled release (2018).
[5] S.C.C. Arruda, A.L.D. Silva, R.M. Galazzi, R.A. Azevedo, M.A.Z. Arruda, Nanoparticles applied to plant science: a review, Talanta 131 (2015) 693-705.
[6] M.R. Maghsoodi, B.A. Lajayer, M. Hatami, M.H. Mirjalili, Challenges and Opportunities of Nanotechnology in Plant-Soil Mediated Systems: Beneficial Role, Phytotoxicity, and Phytoextraction, Advances in Phytonanotechnology, Elsevier2019, pp. 379-404.
[7] V. Ghormade, M.V. Deshpande, K.M. Paknikar, Perspectives for nano-biotechnology enabled protection and nutrition of plants, Biotechnology advances 29(6) (2011) 792-803.
[8] M. Ghosh, A. Jana, S. Sinha, M. Jothiramajayam, A. Nag, A. Chakraborty, A. Mukherjee, A. Mukherjee, Effects of ZnO nanoparticles in plants: cytotoxicity, genotoxicity, deregulation of antioxidant defenses, and cell-cycle arrest, Mutation Research/Genetic Toxicology and Environmental Mutagenesis 807 (2016) 25-32.
[9] M. Kah, T. Hofmann, Nanopesticide research: current trends and future priorities, Environment international 63 (2014) 224-235.
[10] R. Prasad, V. Kumar, K.S. Prasad, Nanotechnology in sustainable agriculture: present concerns and future aspects, African Journal of Biotechnology 13(6) (2014) 705-713.
[11] A. Elizabath, M. Babychan, A.M. Mathew, G.M. Syriac, Application of Nanotechnology in Agriculture, Int. J. Pure App. Biosci 7(2) (2019) 131-139.
[12] T.A. Wani, F. Masoodi, W.N. Baba, M. Ahmad, N. Rahmanian, S.M. Jafari, Nanoencapsulation of Agrochemicals, Fertilizers, and Pesticides for Improved Plant Production, Advances in Phytonanotechnology, Elsevier2019, pp. 279-298.
[13] S. Baker, S. Satish, N. Prasad, R.S. Chouhan, Nano-agromaterials: Influence on plant growth and crop protection, Industrial Applications of Nanomaterials, Elsevier2019, pp. 341-363.
[14] R. Raliya, R. Nair, S. Chavalmane, W.-N. Wang, P. Biswas, Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (Solanum lycopersicum L.) plant, Metallomics 7(12) (2015) 1584-1594.
[15] T. Eichert, A. Kurtz, U. Steiner, H.E. Goldbach, Size exclusion limits and lateral heterogeneity of the stomatal foliar uptake pathway for aqueous solutes and water-suspended nanoparticles, Physiologia Plantarum 134(1) (2008) 151-160.
[16] Y. Shang, M. Hasan, G.J. Ahammed, M. Li, H. Yin, J. Zhou, Applications of Nanotechnology in Plant Growth and Crop Protection: A Review, Molecules 24(14) (2019) 2558.
[17] R.C. Choudhary, S. Kumari, R. Kumaraswamy, G. Sharma, A. Kumar, S. Budhwar, A. Pal, R. Raliya, P. Biswas, Chitosan Nanomaterials for Smart Delivery of Bioactive Compounds in Agriculture, Nanoscale Engineering in Agricultural Management (2019) 124.
[18] F. Sopeña, C. Maqueda, E. Morillo, Controlled release formulations of herbicides based on micro-encapsulation, Ciencia e investigación agraria 36(1) (2009) 27-42.
[19] K. Tsuji, Microencapsulation of pesticides and their improved handling safety, Journal of microencapsulation 18(2) (2001) 137-147.
[20] O. Cota-Arriola, M. Onofre Cortez-Rocha, A. Burgos-Hernández, J. Marina Ezquerra-Brauer, M. Plascencia-Jatomea, Controlled release matrices and micro/nanoparticles of chitosan with antimicrobial potential: development of new strategies for microbial control in agriculture, Journal of the Science of Food and Agriculture 93(7) (2013) 1525-1536.

[21] K. Kurita, Chitin and chitosan: functional biopolymers from marine crustaceans, Marine Biotechnology 8(3) (2006) 203.
[22] S. Şenel, S.J. McClure, Potential applications of chitosan in veterinary medicine, Advanced drug delivery reviews 56(10) (2004) 1467-1480.
[23] P.L. Kashyap, X. Xiang, P. Heiden, Chitosan nanoparticle based delivery systems for sustainable agriculture, International journal of biological macromolecules 77 (2015) 36-51.
[24] V. Zargar, M. Asghari, A. Dashti, A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications, ChemBioEng Reviews 2(3) (2015) 204-226.
[25] R. Sharif, M. Mujtaba, M. Ur Rahman, A. Shalmani, H. Ahmad, T. Anwar, D. Tianchan, X. Wang, The multifunctional role of chitosan in horticultural crops; a review, Molecules 23(4) (2018) 872.
[26] M. Kaya, M. Mujtaba, H. Ehrlich, A.M. Salaberria, T. Baran, C.T. Amemiya, R. Galli, L. Akyuz, I. Sargin, J. Labidi, On chemistry of γ-chitin, Carbohydrate polymers 176 (2017) 177-186.
[27] M.K. Jang, B.G. Kong, Y.I. Jeong, C.H. Lee, J.W. Nah, Physicochemical characterization of α-chitin, β-chitin, and γ-chitin separated from natural resources, Journal of Polymer Science Part A: Polymer Chemistry 42(14) (2004) 3423-3432.
[28] P. Beaney, J. Lizardi-Mendoza, M. Healy, Comparison of chitins produced by chemical and bioprocessing methods, Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology 80(2) (2005) 145-150.
[29] S. Chopra, S. Mahdi, J. Kaur, Z. Iqbal, S. Talegaonkar, F.J. Ahmad, Advances and potential applications of chitosan derivatives as mucoadhesive biomaterials in modern drug delivery, Journal of Pharmacy and Pharmacology 58(8) (2006) 1021-1032.
[30] M. Mujtaba, R.E. Morsi, G. Kerch, M.Z. Elsabee, M. Kaya, J. Labidi, K.M. Khawar, Current advancements in chitosan-based film production for food technology; A review, International journal of biological macromolecules (2018).
[31] A.N. Hernandez-Lauzardo, S. Bautista-Baños, M.G. Velazquez-Del Valle, M. Méndez-Montealvo, M. Sánchez-Rivera, L.A. Bello-Perez, Antifungal effects of chitosan with different molecular weights on in vitro development of Rhizopus stolonifer (Ehrenb.: Fr.) Vuill, Carbohydrate Polymers 73(4) (2008) 541-547.
[32] T. Sun, D. Zhou, J. Xie, F. Mao, Preparation of chitosan oligomers and their antioxidant activity, European Food Research and Technology 225(3-4) (2007) 451-456.
[33] I. Aranaz, M. Mengíbar, R. Harris, Pa nos I, Miralles B, Acosta N, et al, Functional characterization of chitin and chitosan. Curr Chem Biol 3 (2009) 203-30.
[34] M. Yadav, P. Goswami, K. Paritosh, M. Kumar, N. Pareek, V. Vivekanand, Seafood waste: A source for preparation of commercially employable chitin/chitosan materials, Bioresources and Bioprocessing 6(1) (2019) 8.
[35] M.P. Crespo, M.V. Martínez, J.L. Hernández, M.L. Yusty, High-performance liquid chromatographic determination of chitin in the snow crab, Chionoecetes opilio, Journal of Chromatography A 1116(1-2) (2006) 189-192.
[36] S. Das, E.A. Ganesh, Extraction of chitin from trash crabs (Podophthalmus vigil) by an eccentric method, Curr. Res. Biol. Sci. 2(1) (2010) 72-75.
[37] S.V. Sperstad, T. Haug, V. Paulsen, T.M. Rode, G. Strandskog, S.T. Solem, O.B. Styrvold, K. Stensvåg, Characterization of crustins from the hemocytes of the spider crab, Hyas araneus, and the red king crab, Paralithodes camtschaticus, Developmental & Comparative Immunology 33(4) (2009) 583-591.
[38] S. Hajji, I. Younes, O. Ghorbel-Bellaaj, R. Hajji, M. Rinaudo, M. Nasri, K. Jellouli, Structural differences between chitin and chitosan extracted from three different marine sources, International journal of biological macromolecules 65 (2014) 298-306.
[39] M. Kaya, O. Seyyar, T. Baran, S. Erdoğan, M. Kar, A physicochemical characterization of fully acetylated chitin structure isolated from two spider species: With new surface morphology, International journal of biological macromolecules 65 (2014) 553-558.
[40] G.J. Davies, D.P. Knight, F. Vollrath, Chitin in the silk gland ducts of the spider Nephila edulis and the silkworm Bombyx mori, PloS one 8(8) (2013) e73225.

[41] J. Synowiecki, N.A.A.Q. Al-Khateeb, Mycelia of Mucor rouxii as a source of chitin and chitosan, Food Chemistry 60(4) (1997) 605-610.
[42] T. Yu, L. Wang, Y. Yin, Y. Wang, X. Zheng, Effect of chitin on the antagonistic activity of Cryptococcus laurentii against Penicillium expansum in pear fruit, International journal of food microbiology 122(1-2) (2008) 44-48.
[43] R. Kollár, B.B. Reinhold, E. Petráková, H.J. Yeh, G. Ashwell, J. Drgonová, J.C. Kapteyn, F.M. Klis, E. Cabib, Architecture of the yeast cell wall β (1→ 6)-glucan interconnects mannoprotein, β (1→ 3)-glucan, and chitin, Journal of Biological Chemistry 272(28) (1997) 17762-17775.
[44] N.K. Mathur, C.K. Narang, Chitin and chitosan, versatile polysaccharides from marine animals, Journal of Chemical Education 67(11) (1990) 938.
[45] V. Chobot, J. Kremenak, L. Opletal, Phytotherapeutic aspects of diseases of the circulatory system. 4. Chitin and chitosan, Ceska a Slovenska farmacie: casopis Ceske farmaceuticke spolecnosti a Slovenske farmaceuticke spolecnosti 44(4) (1995) 190-195.
[46] M. Kaya, M. Asan-Ozusaglam, S. Erdogan, Comparison of antimicrobial activities of newly obtained low molecular weight scorpion chitosan and medium molecular weight commercial chitosan, Journal of bioscience and bioengineering 121(6) (2016) 678-684.
[47] E.S. Abdou, K.S. Nagy, M.Z. Elsabee, Extraction and characterization of chitin and chitosan from local sources, Bioresource Technology 99(5) (2008) 1359-1367.
[48] M. Mahlous, D. Tahtat, S. Benamer, A.N. Khodja, Gamma irradiation-aided chitin/chitosan extraction from prawn shells, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 265(1) (2007) 414-417.
[49] M. Zhang, A. Haga, H. Sekiguchi, S. Hirano, Structure of insect chitin isolated from beetle larva cuticle and silkworm (Bombyx mori) pupa exuvia, International Journal of Biological Macromolecules 27(1) (2000) 99-105.
[50] M. Kaya, Y.S. Cakmak, T. Baran, M. Asan-Ozusaglam, A. Mentes, K.O. Tozak, New chitin, chitosan, and O-carboxymethyl chitosan sources from resting eggs of Daphnia longispina (Crustacea); with physicochemical characterization, and antimicrobial and antioxidant activities, Biotechnology and bioprocess engineering 19(1) (2014) 58-69.
[51] M. Kaya, T. Baran, A. Mentes, M. Asaroglu, G. Sezen, K.O. Tozak, Extraction and characterization of α-chitin and chitosan from six different aquatic invertebrates, Food biophysics 9(2) (2014) 145-157.
[52] G. Chaussard, A. Domard, New aspects of the extraction of chitin from squid pens, Biomacromolecules 5(2) (2004) 559-564.
[53] Y. Fan, T. Saito, A. Isogai, Preparation of chitin nanofibers from squid pen β-chitin by simple mechanical treatment under acid conditions, Biomacromolecules 9(7) (2008) 1919-1923.
[54] A. Roy, S.K. Singh, J. Bajpai, A.K. Bajpai, Controlled pesticide release from biodegradable polymers, Central European Journal of Chemistry 12(4) (2014) 453-469.
[55] A. Mihou, A. Michaelakis, F. Krokos, B. Mazomenos, E. Couladouros, Prolonged slow release of (Z)-11-hexadecenyl acetate employing polyurea microcapsules, Journal of applied entomology 131(2) (2007) 128-133.
[56] O. Cota-Arriola, M. Onofre Cortez-Rocha, A. Burgos-Hernández, J. Marina Ezquerra-Brauer, M. Plascencia-Jatomea, Controlled release matrices and micro/nanoparticles of chitosan with antimicrobial potential: development of new strategies for microbial control in agriculture, Journal of the Science of Food and Agriculture 93(7) (2013) 1525-1536.
[57] S. Şenel, E.A. Aksoy, G. Akca, Application of Chitosan Based Scaffolds for Drug Delivery and Tissue Engineering in Dentistry, Marine-Derived Biomaterials for Tissue Engineering Applications, Springer2019, pp. 157-178.
[58] C.-P. Gong, Y. Luo, Y.-Y. Pan, Novel synthesized zinc oxide nanoparticles loaded alginate-chitosan biofilm to enhanced wound site activity and anti-septic abilities for the management of complicated abdominal wound dehiscence, Journal of Photochemistry and Photobiology B: Biology 192 (2019) 124-130.

[59] A. Manikandan, M. Sathiyabama, Preparation of chitosan nanoparticles and its effect on detached rice leaves infected with Pyricularia grisea, International journal of biological macromolecules 84 (2016) 58-61.

[60] A. Mohammadi, M. Hashemi, S.M. Hosseini, Effect of chitosan molecular weight as micro and nanoparticles on antibacterial activity against some soft rot pathogenic bacteria, LWT-Food Science and Technology 71 (2016) 347-355.

[61] V. Saharan, A. Mehrotra, R. Khatik, P. Rawal, S. Sharma, A. Pal, Synthesis of chitosan based nanoparticles and their in vitro evaluation against phytopathogenic fungi, International journal of biological macromolecules 62 (2013) 677-683.

[62] V. Saharan, G. Sharma, M. Yadav, M.K. Choudhary, S. Sharma, A. Pal, R. Raliya, P. Biswas, Synthesis and in vitro antifungal efficacy of Cu–chitosan nanoparticles against pathogenic fungi of tomato, International journal of biological macromolecules 75 (2015) 346-353.

[63] K. Xing, X. Shen, X. Zhu, X. Ju, X. Miao, J. Tian, Z. Feng, X. Peng, J. Jiang, S. Qin, Synthesis and in vitro antifungal efficacy of oleoyl-chitosan nanoparticles against plant pathogenic fungi, International journal of biological macromolecules 82 (2016) 830-836.

[64] R.C. Choudhary, R. Kumaraswamy, S. Kumari, S. Sharma, A. Pal, R. Raliya, P. Biswas, V. Saharan, Cu-chitosan nanoparticle boost defense responses and plant growth in maize (Zea mays L.), Scientific reports 7(1) (2017) 9754.

[65] M. Sathiyabama, R.E. Charles, Fungal cell wall polymer based nanoparticles in protection of tomato plants from wilt disease caused by Fusarium oxysporum f. sp. lycopersici, Carbohydrate polymers 133 (2015) 400-407.

[66] R. Kumaraswamy, S. Kumari, R.C. Choudhary, A. Pal, R. Raliya, P. Biswas, V. Saharan, Engineered chitosan based nanomaterials: bioactivities, mechanisms and perspectives in plant protection and growth, International journal of biological macromolecules 113 (2018) 494-506.

[67] Y. Ohya, M. Shiratani, H. Kobayashi, T. Ouchi, Release behavior of 5-fluorouracil from chitosan-gel nanospheres immobilizing 5-fluorouracil coated with polysaccharides and their cell specific cytotoxicity, Journal of Macromolecular Science—Pure and Applied Chemistry 31(5) (1994) 629-642.

[68] P. Calvo, C. Remunan-Lopez, J.L. Vila-Jato, M. Alonso, Novel hydrophilic chitosan-polyethylene oxide nanoparticles as protein carriers, Journal of Applied Polymer Science 63(1) (1997) 125-132.

[69] S. Mitra, U. Gaur, P. Ghosh, A. Maitra, Tumour targeted delivery of encapsulated dextran–doxorubicin conjugate using chitosan nanoparticles as carrier, Journal of Controlled Release 74(1-3) (2001) 317-323.

[70] S.A. Agnihotri, N.N. Mallikarjuna, T.M. Aminabhavi, Recent advances on chitosan-based micro- and nanoparticles in drug delivery, Journal of controlled release 100(1) (2004) 5-28.

[71] S.A. Agnihotri, T.M. Aminabhavi, Controlled release of clozapine through chitosan microparticles prepared by a novel method, Journal of Controlled Release 96(2) (2004) 245-259.

[72] H. Tokumitsu, H. Ichikawa, Y. Fukumori, Chitosan-gadopentetic acid complex nanoparticles for gadolinium neutron-capture therapy of cancer: preparation by novel emulsion-droplet coalescence technique and characterization, Pharmaceutical research 16(12) (1999) 1830-1835.

[73] S. Davis, L. Illum, Sustained release chitosan microspheres prepared by novel spray drying methods, Journal of microencapsulation 16(3) (1999) 343-355.

[74] A. Grenha, Chitosan nanoparticles: a survey of preparation methods, Journal of drug targeting 20(4) (2012) 291-300.

[75] W. Tiyaboonchai, Chitosan nanoparticles: a promising system for drug delivery, วารสาร มหาวิทยาลัย นเรศวร: วิทยาศาสตร์ และ เทคโนโลยี 11(3) (2013) 51-66.

[76] N. Kildeeva, P. Perminov, L. Vladimirov, V. Novikov, S. Mikhailov, About mechanism of chitosan cross-linking with glutaraldehyde, Russian journal of bioorganic chemistry 35(3) (2009) 360-369.

[77] K. Janes, P. Calvo, M. Alonso, Polysaccharide colloidal particles as delivery systems for macromolecules, Advanced drug delivery reviews 47(1) (2001) 83-97.

[78] J. Antoniou, F. Liu, H. Majeed, J. Qi, W. Yokoyama, F. Zhong, Physicochemical and morphological properties of size-controlled chitosan–tripolyphosphate nanoparticles, Colloids and Surfaces A: Physicochemical and Engineering Aspects 465 (2015) 137-146.

[79] C.C. Sipoli, N. Santana, A.A.M. Shimojo, A. Azzoni, L.G. de la Torre, Scalable production of highly concentrated chitosan/TPP nanoparticles in different pHs and evaluation of the in vitro transfection efficiency, Biochemical engineering journal 94 (2015) 65-73.
[80] S. Song, Y. Wang, J. Xie, B. Sun, N. Zhou, H. Shen, J. Shen, Carboxymethyl Chitosan Modified Carbon Nanoparticle for Controlled Emamectin Benzoate Delivery: Improved Solubility, pH-Responsive Release, and Sustainable Pest Control, ACS Applied Materials & Interfaces 11(37) (2019) 34258-34267.
[81] J. Tang, G. Ding, J. Niu, W. Zhang, G. Tang, Y. Liang, C. Fan, H. Dong, J. Yang, J. Li, Y. Cao, Preparation and characterization of tebuconazole metal-organic framework-based microcapsules with dual-microbicidal activity, Chemical Engineering Journal 359 (2019) 225-232.
[82] P. Rychter, Chitosan/glyphosate formulation as a potential, environmental friendly herbicide with prolonged activity, Journal of Environmental Science and Health, Part B 54(8) (2019) 681-692.
[83] A. Kamari, N.F.A. Aljafree, S.N.M. Yusoff, N,N-dimethylhexadecyl carboxymethyl chitosan as a potential carrier agent for rotenone, International Journal of Biological Macromolecules 88 (2016) 263-272.
[84] S. Yusoff, A. Kamari, S. Ishak, A. Halim, N-hexanoyl-O-glycol chitosan as a carrier agent for water-insoluble herbicide, Journal of Physics: Conference Series, IOP Publishing, 2018, p. 012053.
[85] Z. Ahmadi, M. Saber, M. Bagheri, G.R. Mahdavinia, Achillea millefolium essential oil and chitosan nanocapsules with enhanced activity against Tetranychus urticae, Journal of Pest Science 91(2) (2018) 837-848.
[86] Y. Xiang, G. Zhang, Y. Chi, D. Cai, Z. Wu, Fabrication of a controllable nanopesticide system with magnetic collectability, Chemical Engineering Journal 328 (2017) 320-330.
[87] A. Cabrera, R. Celis, M.C. Hermosín, Imazamox–clay complexes with chitosan-and iron (III)-modified smectites and their use in nanoformulations, Pest management science 72(7) (2016) 1285-1294.
[88] M. Rashidipour, A. Maleki, S. Kordi, M. Birjandi, N. Pajohi, E. Mohamadi, R. Heydari, R. Rezaee, B. Rasoulian, B. Davari, Pectin/Chitosan/Tripolyphosphate Nanoparticles: Efficient Carriers for Reducing Soil Sorption, Cytotoxicity and Mutagenicity of Paraquat and Enhancement of its Herbicide Activity, Journal of agricultural and food chemistry (2019).
[89] N.M. Silveira, A.B. Seabra, F.C.C. Marcos, M.T. Pelegrino, E.C. Machado, R.V. Ribeiro, Encapsulation of S-nitrosoglutathione into chitosan nanoparticles improves drought tolerance of sugarcane plants, Nitric Oxide 84 (2019) 38-44.
[90] R.V. Kumaraswamy, S. Kumari, R.C. Choudhary, S.S. Sharma, A. Pal, R. Raliya, P. Biswas, V. Saharan, Salicylic acid functionalized chitosan nanoparticle: A sustainable biostimulant for plant, International Journal of Biological Macromolecules 123 (2019) 59-69.
[91] F.N. Maluin, M.Z. Hussein, N.A. Yusof, S. Fakurazi, A.S. Idris, Z. Hilmi, N. Hailini, L.D. Jeffery Daim, Preparation of Chitosan–Hexaconazole Nanoparticles as Fungicide Nanodelivery System for Combating Ganoderma Disease in Oil Palm, Molecules 24(13) (2019) 2498.
[92] N.K. Kalagatur, N. Ghosh, O. Sivaraman, N. Sundararaj, Antifungal activity of chitosan nanoparticles encapsulated with Cymbopogon martinii essential oil on plant pathogenic fungi Fusarium graminearum, Frontiers in pharmacology 9 (2018) 610.
[93] N.S. Khalifa, M.N. Hasaneen, The effect of chitosan–PMAA–NPK nanofertilizer on Pisum sativum plants, 3 Biotech 8(4) (2018) 193.
[94] A. Pereira, I. Sandoval-Herrera, S. Zavala-Betancourt, H. Oliveira, A. Ledezma-Pérez, J. Romero, L. Fraceto, γ-Polyglutamic acid/chitosan nanoparticles for the plant growth regulator gibberellic acid: Characterization and evaluation of biological activity, Carbohydrate polymers 157 (2017) 1862-1873.
[95] A.E. Santo Pereira, P.M. Silva, J.L. Oliveira, H.C. Oliveira, L.F. Fraceto, Chitosan nanoparticles as carrier systems for the plant growth hormone gibberellic acid, Colloids and Surfaces B: Biointerfaces 150 (2017) 141-152.
[96] Z. Souri, N. Karimi, M. Sarmadi, E. Rostami, Salicylic acid nanoparticles (SANPs) improve growth and phytoremediation efficiency of Isatis cappadocica Desv., under As stress, IET Nanobiotechnology 11(6) (2017) 650-655.

[97] S. Martin-Saldaña, M.T. Chevalier, M.J. Iglesias, S.L. Colman, C.A. Casalongué, V.A. Álvarez, A.A. Chevalier, Salicylic acid loaded chitosan microparticles applied to lettuce seedlings: recycling shrimp fishing industry waste, Carbohydrate polymers 200 (2018) 321-331.
[98] R.C. Choudhary, R. Kumaraswamy, S. Kumari, S. Sharma, A. Pal, R. Raliya, P. Biswas, V. Saharan, Zinc encapsulated chitosan nanoparticle to promote maize crop yield, International journal of biological macromolecules 127 (2019) 126-135.
[99] B.R. Araújo, L.P. Romão, M.E. Doumer, A.S. Mangrich, Evaluation of the interactions between chitosan and humics in media for the controlled release of nitrogen fertilizer, Journal of environmental management 190 (2017) 122-131.
[100] N.M.C. Ha, T.H. Nguyen, S.-L. Wang, A.D. Nguyen, Preparation of NPK nanofertilizer based on chitosan nanoparticles and its effect on biophysical characteristics and growth of coffee in green house, Research on Chemical Intermediates 45(1) (2019) 51-63.
[101] H.M. Abdel-Aziz, M.N. Hasaneen, A.M. Omer, Nano chitosan-NPK fertilizer enhances the growth and productivity of wheat plants grown in sandy soil, Spanish Journal of Agricultural Research 14(1) (2016) 0902.
[102] B.R. dos Santos, F.B. Bacalhau, T. dos Santos Pereira, C.F. Souza, R. Faez, Chitosan-montmorillonite microspheres: a sustainable fertilizer delivery system, Carbohydrate polymers 127 (2015) 340-346.
[103] M.M. Iftime, G.L. Ailiesei, E. Ungureanu, L. Marin, Designing chitosan based eco-friendly multifunctional soil conditioner systems with urea controlled release and water retention, Carbohydrate polymers 223 (2019) 115040.
[104] J. Perez, N. Francois, G. Maroniche, M. Borrajo, M. Pereyra, C. Creus, A novel, green, low-cost chitosan-starch hydrogel as potential delivery system for plant growth-promoting bacteria, Carbohydrate polymers 202 (2018) 409-417.
[105] P. Wang, F.-J. Zhao, P.M. Kopittke, Engineering Crops without Genome Integration Using Nanotechnology, Trends in plant science (2019).
[106] S.-Y. Kwak, T.T.S. Lew, C.J. Sweeney, V.B. Koman, M.H. Wong, K. Bohmert-Tatarev, K.D. Snell, J.S. Seo, N.-H. Chua, M.S. Strano, Chloroplast-selective gene delivery and expression in planta using chitosan-complexed single-walled carbon nanotube carriers, Nature nanotechnology 14(5) (2019) 447.
[107] Y. Wu, J.A. Phillips, H. Liu, R. Yang, W. Tan, Carbon nanotubes protect DNA strands during cellular delivery, ACS nano 2(10) (2008) 2023-2028.
[108] E. Dong, Z. Yang, C. Zhou, C. Wang, S. Li, Q. Ouyang, L. Kong, Z. He, J. Xie, P. Li, pH-responsive ultrasonic self-assembly spinosad-loaded nanomicelles and their antifungal activity to Fusarium oxysporum, Reactive and Functional Polymers 141 (2019) 123-132.
[109] X. He, Z. Sun, K. He, S. Guo, Biopolymer microencapsulations of Bacillus thuringiensis crystal preparations for increased stability and resistance to environmental stress, Applied microbiology and biotechnology 101(7) (2017) 2779-2789.
[110] H.C. Paula, F.M. Sombra, R. de Freitas Cavalcante, F.O. Abreu, R.C. de Paula, Preparation and characterization of chitosan/cashew gum beads loaded with Lippia sidoides essential oil, Materials Science and Engineering: C 31(2) (2011) 173-178.
[111] H. Guan, D. Chi, J. Yu, X. Li, A novel photodegradable insecticide: Preparation, characterization and properties evaluation of nano-Imidacloprid, Pesticide Biochemistry and Physiology 92(2) (2008) 83-91.
[112] S.-B. Lao, Z.-X. Zhang, H.-H. Xu, G.-B. Jiang, Novel amphiphilic chitosan derivatives: synthesis, characterization and micellar solubilization of rotenone, Carbohydrate Polymers 82(4) (2010) 1136-1142.
[113] Y. Liang, C. Fan, H. Dong, W. Zhang, G. Tang, J. Yang, N. Jiang, Y. Cao, Preparation of MSNs-chitosan@ prochloraz nanoparticles for reducing toxicity and improving release properties of prochloraz, ACS Sustainable Chemistry & Engineering 6(8) (2018) 10211-10220.

[114] N. Aljafree, A. Kamari, Synthesis, characterisation and potential application of deoxycholic acid carboxymethyl chitosan as a carrier agent for rotenone, Journal of Polymer Research 25(6) (2018) 133.

[115] J. Tang, G. Ding, J. Niu, W. Zhang, G. Tang, Y. Liang, C. Fan, H. Dong, J. Yang, J. Li, Preparation and characterization of tebuconazole metal-organic framework-based microcapsules with dual-microbicidal activity, Chemical Engineering Journal 359 (2019) 225-232.

[116] E.V. Campos, P.L. Proença, J.L. Oliveira, C.C. Melville, J.F. Della Vechia, D.J. De Andrade, L.F. Fraceto, Chitosan nanoparticles functionalized with β-cyclodextrin: a promising carrier for botanical pesticides, Scientific reports 8(1) (2018) 2067.

[117] B. Strandberg, C. Boutin, S.K. Mathiassen, C. Damgaard, Y.L. Dupont, D.J. Carpenter, P. Kudsk, Effects of herbicides on non-target terrestrial plants, Pesticide Dose: Effects on the Environment and Target and Non-Target Organisms, ACS Publications2017, pp. 149-166.

[118] A.d.E. Santo Pereira, H.C. Oliveira, L.F. Fraceto, Polymeric nanoparticles as an alternative for application of gibberellic acid in sustainable agriculture: a field study, Scientific reports 9(1) (2019) 7135.

[119] H.C. Oliveira, B.C. Gomes, M.T. Pelegrino, A.B. Seabra, Nitric oxide-releasing chitosan nanoparticles alleviate the effects of salt stress in maize plants, Nitric Oxide 61 (2016) 10-19.

[120] P. Deshpande, A. Dapkekar, M.D. Oak, K.M. Paknikar, J.M. Rajwade, Zinc complexed chitosan/TPP nanoparticles: a promising micronutrient nanocarrier suited for foliar application, Carbohydrate polymers 165 (2017) 394-401.

[121] S. Muthukrishnan, I. Murugan, M. Selvaraj, Chitosan nanoparticles loaded with thiamine stimulate growth and enhances protection against wilt disease in Chickpea, Carbohydrate polymers 212 (2019) 169-177.

[122] D. França, Â.F. Medina, L.L. Messa, C.F. Souza, R. Faez, Chitosan spray-dried microcapsule and microsphere as fertilizer host for swellable− controlled release materials, Carbohydrate polymers 196 (2018) 47-55.

[123] J.J. Perez, N.J. Francois, Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers, Carbohydrate polymers 148 (2016) 134-142.

[124] M.A. Melaj, M.E. Daraio, A. Vazquez, Controlled release on sand bed columns and biodegradability in soil of chitosan: Hydroxypropyl methylcellulose films, Journal of Applied Polymer Science 136(20) (2019) 47532.

[125] V. Saharan, R. Kumaraswamy, R.C. Choudhary, S. Kumari, A. Pal, R. Raliya, P. Biswas, Cu-chitosan nanoparticle mediated sustainable approach to enhance seedling growth in maize by mobilizing reserved food, Journal of agricultural and food chemistry 64(31) (2016) 6148-6155.

[126] T. Li, S. Lü, J. Yan, X. Bai, C. Gao, M. Liu, An Environment-Friendly Fertilizer Prepared by Layer-by-Layer Self-Assembly for pH-Responsive Nutrient Release, ACS applied materials & interfaces 11(11) (2019) 10941-10950.

[127] D.J.M. Plofino, C.C.P. Brutas, C.G. Alfafara, M.C. Maguyon-Detras, V.P. Migo, Parametric and Optimization Studies on the entrapment of Potassium Fertilizer into Chitosan-Poly (methacrylic acid) Carrier via Ionic Gelation, MATEC Web of Conferences, EDP Sciences, 2019, p. 06009.

[128] M.A. El-Aziz, S. Morsi, D.M. Salama, M. Abdel-Aziz, M.S.A. Elwahed, E. Shaaban, A. Youssef, Preparation and characterization of chitosan/polyacrylic acid/copper nanocomposites and their impact on onion production, International journal of biological macromolecules 123 (2019) 856-865.

[129] O. León, A. Muñoz-Bonilla, D. Soto, J. Ramirez, Y. Marquez, M. Colina, M. Fernández-García, Preparation of oxidized and grafted chitosan superabsorbents for urea delivery, Journal of Polymers and the Environment 26(2) (2018) 728-739.

[130] S.R. Nadendla, T.S. Rani, P.R. Vaikuntapu, R.R. Maddu, A.R. Podile, HarpinPss encapsulation in chitosan nanoparticles for improved bioavailability and disease resistance in tomato, Carbohydrate polymers 199 (2018) 11-19.

[131] A. Kamari, S.N.M. Yusoff, N-octyl chitosan derivatives as amphiphilic carrier agents for herbicide formulations, Open Chemistry 17(1) (2019) 365-380.

[132] C.R. Maruyama, M. Guilger, M. Pascoli, N. Bileshy-José, P. Abhilash, L.F. Fraceto, R. De Lima, Nanoparticles based on chitosan as carriers for the combined herbicides imazapic and imazapyr, Scientific reports 6 (2016) 19768.
[133] R. Grillo, Z. Clemente, J.L. de Oliveira, E.V.R. Campos, V.C. Chalupe, C.M. Jonsson, R. de Lima, G. Sanches, C.S. Nishisaka, A.H. Rosa, Chitosan nanoparticles loaded the herbicide paraquat: The influence of the aquatic humic substances on the colloidal stability and toxicity, Journal of hazardous materials 286 (2015) 562-572.
[134] Z. Yu, X. Sun, H. Song, W. Wang, Z. Ye, L. Shi, K. Ding, Glutathione-responsive carboxymethyl chitosan nanoparticles for controlled release of herbicides, Materials Sciences and Applications 6(06) (2015) 591.
[135] Z. Ye, J. Guo, D. Wu, M. Tan, X. Xiong, Y. Yin, G. He, Photo-responsive shell cross-linked micelles based on carboxymethyl chitosan and their application in controlled release of pesticide, Carbohydrate polymers 132 (2015) 520-528.
[136] C. Xu, L. Cao, P. Zhao, Z. Zhou, C. Cao, F. Li, Q. Huang, Emulsion-based synchronous pesticide encapsulation and surface modification of mesoporous silica nanoparticles with carboxymethyl chitosan for controlled azoxystrobin release, Chemical Engineering Journal 348 (2018) 244-254.
[137] L. Cao, H. Zhang, C. Cao, J. Zhang, F. Li, Q. Huang, Quaternized chitosan-capped mesoporous silica nanoparticles as nanocarriers for controlled pesticide release, Nanomaterials 6(7) (2016) 126.
[138] C. Xu, L. Cao, P. Zhao, Z. Zhou, C. Cao, F. Zhu, F. Li, Q. Huang, Synthesis and characterization of stimuli-responsive poly (2-dimethylamino-ethylmethacrylate)-grafted chitosan microcapsule for controlled pyraclostrobin release, International journal of molecular sciences 19(3) (2018) 854.
[139] H. Yan, X. Chen, Y. Feng, F. Xiang, J. Li, Z. Shi, X. Wang, Q. Lin, Modification of montmorillonite by ball-milling method for immobilization and delivery of acetamiprid based on alginate/exfoliated montmorillonite nanocomposite, Polymer Bulletin 73(4) (2016) 1185-1206.
[140] S. Kumar, N. Chauhan, M. Gopal, R. Kumar, N. Dilbaghi, Development and evaluation of alginate–chitosan nanocapsules for controlled release of acetamiprid, International journal of biological macromolecules 81 (2015) 631-637.
[141] N. Chauhan, N. Dilbaghi, M. Gopal, R. Kumar, K.-H. Kim, S. Kumar, Development of chitosan nanocapsules for the controlled release of hexaconazole, International journal of biological macromolecules 97 (2017) 616-624.